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(54) Title: POLYMER COMPOSITIONS COMPRISING CROSSLINKABLE SUBSTANTIALLY RANDOM TERPOLYMERS OF ETHYLENE, PROPYLENE, AND VINYL AROMATIC MONOMERS AND ARTICLES FABRICATED THEREFROM.

(57) Abstract: This invention describes improved compositions comprising crosslinkable substantially random ethylene-propylene vinyl aromatic monomer interpolymers, exemplified by ethylene-propylene-styrene (EPS) interpolymers, and articles fabricated from these compositions. Any known methods of crosslinking may be used (including peroxides, e-beam radiation, silane chemistries and combinations thereof).

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POLYMER COMPOSITIONS COMPRISING CROSSLINKABLE SUBSTANTIALLY RANDOM TERPOLYMERS OF ETHYLENE, PROPYLENE, AND VINYL AROMATIC MONOMERS AND ARTICLES FABRICATED THEREFROM.

5 This invention describes improved compositions comprising crosslinkable substantially random ethylene-propylene vinyl aromatic monomer interpolymers, exemplified by ethylene-propylene-styrene (EPS) interpolymers, and articles fabricated from these compositions. Any known methods of crosslinking may be used (including peroxides, e-beam radiation, silane chemistries and combinations thereof).

10 The generic class of materials covered by  $\alpha$ -olefin/vinyl aromatic monomer interpolymers, and especially ethylene/styrene interpolymers and copolymers, are known in the art. They offer a range of material structures and properties which makes them useful for varied applications, such as compatibilizers for blends of polyethylene and polystyrene, as described in US 5,460,818. Although of utility in their own right, industry is constantly seeking to improve the applicability of these  
15 interpolymers.

U.S. Patent No. 4,935,466 discloses block copolymers comprising a monoalkenylaromatic hydrocarbon block and a hydrogenated conjugated diene hydrocarbon block which are grafted at the aromatic groups, by reacting the block copolymer with an azide.

U.S. Patent Nos. 5,883,144 and 6,103,775 discloses cross-linked polymeric foam  
20 compositions which utilize cross-linked polyolefin copolymers and show improvements in strength, toughness, flexibility, heat resistance and heat-sealing temperature ranges as compared to conventional low density polyethylene compositions. The new compositions also show processing improvements over linear low density polyethylene. The novel polyolefins, which are essentially linear, comprise ethylene polymerized with at least one unsaturated  $C_3$  to  $C_{20}$  alpha-olefinic  
25 comonomer, and optionally at least one  $C_3$  to  $C_{20}$  polyene, and exhibit, in an uncross-linked state, a resin density in the range of  $0.86 \text{ g/cm}^3$  to  $0.96 \text{ g/cm}^3$ , a melt index in the range of 0.5 dg/min to 100 dg/min, a molecular weight distribution in the range of from 1.5 to 3.5, and a composition distribution breadth index greater than 45 percent. The polyolefins are silane-grafted to enhance the physical properties and processability of the resins. Slow silane-grafted materials exhibit enhanced physical  
30 and processing properties.

U.S. Patent No. 6,004,647 discloses polymer blends, used both in foamed and unfoamed states as a replacement for conventional EPDM and other elastomers. The composition of the blend included a single-site catalyzed polyolefin resin having a density of below  $0.878 \text{ g/cm}^3$  and up to 40 weight percent of a polyolefin including ethylene and propylene. The polymer blend was cross-linked.

35 The polymer blends are formable and foamable.

U.S. Patent No. 5,859,076 disclosed open cell foamed articles including silane-grafted single-site initiated polyolefin resins. The single-site initiated olefin polymer resin can be a polyethylene, a copolymer of ethylene, a C<sub>3</sub>-C<sub>20</sub> alpha-olefin, or a copolymer of ethylene, a C<sub>3</sub>-C<sub>20</sub> alpha-olefin and a C<sub>4</sub>-C<sub>20</sub> diene. The open cell foamed articles have good cushioning properties and can be non-  
5 allergenic.

Although peroxide or high-energy radiation can be used to crosslink polyethylene, the prior art suggests that polymers with tertiary hydrogen (such as polypropylene or polystyrene) undergo chain scission rather than crosslinking when they are treated with peroxide or electron beam (e-beam) radiation. In the case of ethylene/styrene interpolymers, the rate and degree of crosslinking decreases  
10 with increasing amounts of styrene in the copolymer. Surprisingly, we have found that the use of substantially random ethylene-propylene-styrene (EPS) terpolymers results in significantly improved crosslinking, with key properties such as thermal stability, compression set, paintability and printability remaining acceptable. We have surprisingly found that EPS terpolymers can be effectively crosslinked using peroxide, e-beam radiation, and silane chemistries. The resulting  
15 partially or fully crosslinked interpolymers have higher upper service temperature and are less sticky than the unmodified polymers. This radical chemistry can also be used to prepare EPS resins that exhibit improved melt strength and processability.

The present invention also includes blends of substantially random interpolymers with one or more additional other polymers in which the copolymer is at least partially crosslinked. The  
20 additional polymers include homopolymer and copolymers of C<sub>2</sub>-C<sub>20</sub>  $\alpha$ -olefin monomers, ethylene-styrene copolymers, ethylene vinyl acetate copolymers (EVA), styrenic homopolymers and copolymers, and elastomers such as those containing unsaturated vinyl groups.

Compared with the use of other ethylenic polymers (homopolymers, copolymers and interpolymers) known in the prior art, the crosslinked compositions and fabricated articles of this  
25 invention exhibit one or more of the following improvements; faster crosslinking, more effective or complete crosslinking, reduced chain scission, increased thermal stability, lower modulus, increased upper service temperature (UST), decreased compression set, increased resiliency, and increased impact energy absorption.

The compositions of this invention may be fabricated and shaped in a variety of ways,  
30 preferably in a melt processing operation. The fabricated articles include films, including as a layer in a multi-layer film structure, and sheet produced by calendering, blow molding, casting, (co-)extrusion or extrusion casting operations, foams, roofing membranes, wire and cable, insulations, gaskets, hoses and belts, footwear, automotive parts and trim, injection molded parts and other applications that require elastomeric materials. Additives (such as nucleating agents, antioxidants, pigments, fire-

retardants, etc) may be added to the polymer compositions and fabricated articles produced from the polymer compositions

The present invention pertains to a polymer composition comprising;

- 1) from 0.5 to 100 percent by weight (based on the combined weight of Components 1, 2  
5 and 3) of one or more crosslinkable substantially random interpolymers comprising;
  - a) from 0.5 to 65 mol percent of polymer units derived from at least one vinyl aromatic monomer,
  - b) from 1 to 99 mol percent of polymer units derived from ethylene or ethylene in combination with one or more C<sub>4</sub>-C<sub>20</sub>  $\alpha$ -olefins;
  - 10 c) from 0.5 to 80 mol percent of polymer units derived from propylene; and
  - d) from 0 to 20 mol percent of polymer units derived from one or more of ethylenically unsaturated polymerizable monomers other than those derived from (a) and (b); and;
- (2) from 0 to 99.5 percent by weight (based on the combined weight of Components 1, 2 and  
15 3) of one or more thermoplastics other than Component 1.
- (3) from 0 to 90 percent by weight (based on the combined weight of Components 1, 2 and 3) of one or more fillers.

All references herein to elements or metals belonging to a certain Group refer to the Periodic Table of the Elements published and copyrighted by CRC Press, Inc., 1989. Also any reference to the  
20 Group or Groups shall be to the Group or Groups as reflected in this Periodic Table of the Elements using the IUPAC system for numbering groups.

Any numerical values recited herein include all values from the lower value to the upper value in increments of one unit provided that there is a separation of at least 2 units between any lower value and any higher value. As an example, if it is stated that the amount of a component or a  
25 value of a process variable such as, for example, temperature, pressure, time is, for example, from 1 to 90, preferably from 20 to 80, more preferably from 30 to 70, it is intended that values such as 15 to 85, 22 to 68, 43 to 51, 30 to 32 etc. are expressly enumerated in this specification. For values which are less than one, one unit is considered to be 0.0001, 0.001, 0.01 or 0.1 as appropriate. These are only examples of what is specifically intended and all possible combinations of numerical values  
30 between the lowest value and the highest value enumerated are to be considered to be expressly stated in this application in a similar manner.

The term "substantially random" in the substantially random interpolymers comprising polymer units derived from ethylene or ethylene in combination with one or more  $\alpha$ -olefin monomers with one or more vinyl aromatic monomers as used herein means that the distribution of the  
35 monomers of said interpolymers can be described by the Bernoulli statistical model or by a first or

second order Markovian statistical model, as described by J. C. Randall in POLYMER SEQUENCE DETERMINATION, Carbon-13 NMR Method, Academic Press New York, 1977, pp. 71-78.

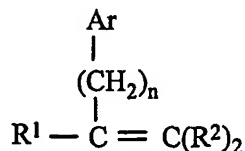
Preferably, substantially random interpolymers do not contain more than 15 percent of the total amount of vinyl aromatic monomer in blocks of vinyl aromatic monomer of more than 3 units. This means that in the carbon-<sup>13</sup> NMR spectrum of the substantially random interpolymers the peak areas corresponding to the main chain methylene and methine carbons representing either meso diad sequences or racemic diad sequences should not exceed 75 percent of the total peak area of the main chain methylene and methine carbons.

The term "crosslinkable substantially random interpolymers" means a substantially random interpolymers containing from 0.5 to 65, preferably from 1 to 50, and most preferably from 1 to 45 mole percent of polymer units derived from one or more vinyl aromatic monomers, especially styrene; and from 1 to 99, preferably from 20 to 98 and most preferably from 30 to 98 mole percent of polymer units derived from ethylene or ethylene in combination with one or more C<sub>4</sub>-C<sub>20</sub> α-olefins; and from 0.5 to 80, preferably from 1 to 50 and most preferably from 1 to 45 mole percent of polymer units derived from propylene; and, optionally from 0 to 20 mole percent of polymer units derived from one or more of ethylenically unsaturated polymerizable monomers, such as a diene.

The substantially random interpolymers of the present invention are prepared by polymerizing i) ethylene, or ethylene in combination with one or more C<sub>4</sub> to C<sub>20</sub> α-olefin monomers and ii) propylene, and iii) one or more vinyl aromatic monomers, and optionally iv) other polymerizable ethylenically unsaturated monomer(s).

Suitable α-olefins include for example, α-olefins containing from 4 to 20, preferably from 4 to 12, more preferably from 4 to 8 carbon atoms. Particularly suitable are butene-1, pentene-1, 4-methyl-1-pentene, hexene-1 or octene-1 or ethylene in combination with one or more of propylene, pentene-1, butene-1, 4-methyl-1-pentene, hexene-1 or octene-1. These α-olefins do not contain an aromatic moiety.

Suitable vinyl aromatic monomers, which can be employed to prepare the interpolymers, include, for example, those represented by the following formula:



wherein R<sup>1</sup> is selected from the group of radicals consisting of hydrogen and alkyl radicals containing from 1 to 4 carbon atoms, preferably hydrogen or methyl; each R<sup>2</sup> is independently selected from the group of radicals consisting of hydrogen and alkyl radicals containing from 1 to 4 carbon atoms,

preferably hydrogen or methyl; Ar is a phenyl group or a phenyl group substituted with from 1 to 5 substituents selected from the group consisting of halo, C<sub>1-4</sub>-alkyl, and C<sub>1-4</sub>-haloalkyl; and n has a value from zero to 4, preferably from zero to 2, most preferably zero. Exemplary vinyl aromatic monomers include styrene, vinyl toluene,  $\alpha$ -methylstyrene, t-butyl styrene, chlorostyrene, including  
5 all isomers of these compounds. Particularly suitable such monomers include styrene and lower alkyl- or halogen-substituted derivatives thereof. Preferred monomers include styrene,  $\alpha$ -methyl styrene, the lower alkyl- (C<sub>1</sub> - C<sub>4</sub>) or phenyl-ring substituted derivatives of styrene, such as for example, ortho-, meta-, and para-methylstyrene, the ring halogenated styrenes, para-vinyl toluene or mixtures thereof. A more preferred aromatic vinyl monomer is styrene.

10 Other optional polymerizable ethylenically unsaturated monomer(s) include norbornene and C<sub>1-10</sub> alkyl or C<sub>6-10</sub> aryl substituted norbornenes. Further, one or more dienes can optionally be incorporated into the interpolymer to provide functional sites of unsaturation on the interpolymer useful, for example, to participate in crosslinking reactions. While conjugated dienes such as butadiene, 1,3-pentadiene (that is, piperylene), or isoprene may be used for this purpose,  
15 nonconjugated dienes are preferred. Typical nonconjugated dienes include, for example the open-chain nonconjugated diolefins such as 1,4-hexadiene (see U.S. Patent No. 2,933,480) and 7-methyl-1,6-octadiene (also known as MOCD); cyclic dienes; bridged ring cyclic dienes, such as dicyclopentadiene (see U.S. Patent No. 3,211,709); or alkylidenenorbornenes, such as methylenenorbornene or ethylenenorbornene (see U.S. Patent No. 3,151,173). The nonconjugated  
20 dienes are not limited to those having only two double bonds, but rather also include those having three or more double bonds.

The diene is incorporated in the substantially random interpolymers of the invention in an amount of from 0 to 15 weight percent based on the total weight of the interpolymer. When a diene is employed, it will preferably be provided in an amount of at least 2 weight percent, more preferably at  
25 least 3 weight percent, and most preferably at least 5 weight percent, based on the total weight of the interpolymer. Likewise, when a diene is employed, it will be provided in an amount of no more than 15, preferably no more than 12 weight percent based on the total weight of the interpolymer.

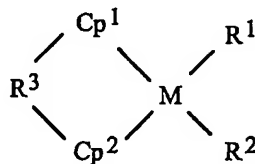
The most preferred substantially random interpolymers are the ethylene/propylene/ styrene, ethylene/propylene/styrene/norbornene, and ethylene/propylene/styrene/diene interpolymers.

30 The substantially random interpolymers include the pseudo-random interpolymers as described in EP-A-0,416,815 B1 and EP-A-0,765,888 by James C. Stevens et al. and US Patent No. 5,703,187 by Francis J. Timmers. The substantially random interpolymers also include the interpolymers of ethylene, olefinic monomers and vinyl aromatic monomers as

described in US Patent No. 5,872,201 by Yunwa W. Cheung et al. The substantially random  
interpolymers can be prepared by polymerizing a mixture of polymerizable monomers in the  
presence of one or more metallocene or constrained geometry catalysts in combination with  
various cocatalysts. Preferred operating conditions for such polymerization reactions are  
5 pressures from atmospheric up to 3000 atmospheres and temperatures from -30°C to 200°C  
as described in US Patent Nos 6,048,909 and 6,231,795 B1. Polymerizations and unreacted  
monomer removal at temperatures above the autopolymerization temperature of the  
respective monomers may result in formation of some amounts of homopolymer  
polymerization products resulting from free radical polymerization.

10 Examples of suitable catalysts, co catalysts, and methods for preparing the  
substantially random interpolymers are disclosed in U.S. Patents: 5,055,438; 5,057,475;  
5,096,867; 5,064,802; 5,132,380; 5,189,192; 5,321,106; 5,347,024; 5,350,723; 5,374,696;  
5,399,635; 5,470,993; 5,703,187; 5,721,185; 5,866,704; 5,959,047; 5,919,983; 6,015,868,  
6,118,013 and 6,150,297.

15 The substantially random  $\alpha$ -olefin/vinyl aromatic interpolymers can also be prepared by the  
methods described in JP 07/278230 employing compounds shown by the general formula



where  $\text{Cp}^1$  and  $\text{Cp}^2$  are cyclopentadienyl groups, indenyl groups, fluorenyl groups, or substituents of  
these, independently of each other;  $\text{R}^1$  and  $\text{R}^2$  are hydrogen atoms, halogen atoms, hydrocarbon  
20 groups with carbon numbers of 1-12, alkoxyl groups, or aryloxyl groups, independently of each other;  
 $\text{M}$  is a group IV metal, preferably Zr or Hf, most preferably Zr; and  $\text{R}^3$  is an alkylene group or  
silanediyl group used to cross-link  $\text{Cp}^1$  and  $\text{Cp}^2$ .

The substantially random  $\alpha$ -olefin/vinyl aromatic interpolymers can also be prepared by the  
methods described by John G. Bradfute et al. (W. R. Grace & Co.) in WO 95/32095; by R. B. Pannell  
25 (Exxon Chemical Patents, Inc.) in WO 94/00500; and in Plastics Technology, p. 25 (September  
1992).

Also suitable are the substantially random interpolymers which comprise at least one  $\alpha$ -  
olefin/vinyl aromatic/vinyl aromatic/ $\alpha$ -olefin tetrad disclosed in U. S. Patent 6,191,245 B1 by Francis  
J. Timmers et al. These interpolymers contain additional signals in their carbon-13 NMR spectra with  
30 intensities greater than three times the peak to peak noise. These signals appear in the chemical shift

range 43.70 - 44.25 ppm and 38.0 - 38.5 ppm. Specifically, major peaks are observed at 44.1, 43.9, and 38.2 ppm. A proton test NMR experiment indicates that the signals in the chemical shift region 43.70 - 44.25 ppm are methine carbons and the signals in the region 38.0 - 38.5 ppm are methylene carbons.

5 Further preparative methods for the interpolymers used in the present invention have been described in the literature. Longo and Grassi (Makromol. Chem., Volume 191, pages 2387 to 2396 [1990]) and D'Anniello et al. (Journal of Applied Polymer Science, Volume 58, pages 1701-1706 [1995]) reported the use of a catalytic system based on methylalumoxane (MAO) and cyclopentadienyltitanium trichloride ( $\text{CpTiCl}_3$ ) to prepare an ethylene-styrene copolymer. Xu and Lin  
10 (Polymer Preprints, Am. Chem. Soc., Div. Polym. Chem.) Volume 35, pages 686,687 [1994]) have reported copolymerization using a  $\text{MgCl}_2/\text{TiCl}_4/\text{NdCl}_3/\text{Al}(\text{iBu})_3$  catalyst to give random copolymers of styrene and propylene. Sernetz and Mulhaupt, (Macromol. Chem. Phys., v. 197, pp. 1071-1083, 1997) have described the influence of polymerization conditions on the copolymerization of styrene with ethylene using  $\text{Me}_2\text{Si}(\text{Me}_4\text{Cp})(\text{N-tert-butyl})\text{TiCl}_2/\text{methylaluminoxane}$  Ziegler-Natta catalysts.  
15 Copolymers of ethylene and styrene produced by bridged metallocene catalysts have been described by Arai, Toshiaki and Suzuki (Polymer Preprints, Am. Chem. Soc., Div. Polym. Chem.) Volume 38, pages 349, 350 [1997]) and in DE 197 11 339 A1 and U.S. Patent No. 5,883,213 to Denki Kagaku Kogyo KK. The manufacture of  $\alpha$ -olefin/vinyl aromatic monomer interpolymers such as propylene/styrene and butene/styrene are described in United States patent number 5,244,996, issued  
20 to Mitsui Petrochemical Industries Ltd.

While preparing the substantially random interpolpolymer, an amount of atactic vinyl aromatic homopolymer may be formed due to homopolymerization of the vinyl aromatic monomer at elevated temperatures. The presence of vinyl aromatic homopolymer is in general not detrimental for the purposes of the present invention and can be tolerated. The vinyl aromatic homopolymer may be  
25 separated from the interpolpolymer, if desired, by extraction techniques such as selective precipitation from solution with a non-solvent for either the interpolpolymer or the vinyl aromatic homopolymer. For the purpose of the present invention it is preferred that no more than 30 weight percent, preferably less than 20 weight percent based on the total weight of the interpolpolymers of atactic vinyl aromatic homopolymer is present.

30 The EPS terpolymers of the present invention may be advantageously used to produce a wide range of fabricated articles including foams, films, including as a layer in a multi-layer film structure, and sheets produced by calendering, blow molding, casting, co-extrusion or extrusion casting operations, compression and injection molded parts, rotational molded parts, fibers. The EPS terpolymers are also useful in applications such as modifiers for bitumen and asphalt compositions, as  
35 components for hot melt and pressure sensitive adhesive systems, extrusion coating, blowmolding,



high speed fiber spinning, oriented nonwovens, thermoforming, labels, candy wrappers, geomembranes, cereal liners, wire and cable, pipes, etc. Preferably the article is formed from a melt of the composition. More preferably it is formed by a melt process. Preferred applications or fabricated articles include wire and cable, footwear and foams.

5       The compositions and fabricated articles of the present invention may comprise blends of EPS terpolymers with one or more other thermoplastics to provide additional improvements in properties including but not limited to processability, upper service temperature, modulus, compressive strength, hardness, toughness and aesthetics of the final fabricated articles (depending on the final blend composition). The blends and fabricated articles will comprise 0.5 to 100, preferably 5  
10   to 100 and most preferably 10 to 100 weight percent of EPS terpolymers (based on total amount of polymers present in the final blend or fabricated article). Examples of the other thermoplastic include, but are not limited to, ethylene styrene interpolymers (ESI), polyethylene, polypropylene (PP), polystyrene (PS), ethylene-propylene rubber and styrene-butadiene rubber. In one embodiment, the EPS terpolymers of the present invention may be further blended with alkenyl aromatic polymers  
15   (such as polystyrene) to make, for example, alkenyl aromatic polymer foams with increased cell size.

The EPS terpolymers of the present invention or their blends with other thermoplastics may be prepared by any suitable means known in the art such as, for example, dry blending in a pelletized form in desired proportions followed by melt blending in an apparatus such as a screw extruder or a Banbury mixer. Dry blended pellets may be directly melt processed into a final solid state article by,  
20   for example, injection molding. The blends may also be made by direct polymerization without isolating blend components. Direct polymerization may use, for example, one or more catalysts in a single reactor or two or more reactors in series or parallel and vary at least one of operating conditions, monomer mixtures and catalyst choice.

The compositions or fabricated articles of the present invention may be cross-linked by any  
25   known cross-linking agent to result in 1 weight percent or greater, preferably 5 weight percent or greater and most preferably 10 weight percent or greater gel based upon the total weight of polymer or fabricated article, as measured according to ASTM D-2765-84, Method A.

The cross-linking processes include, but are not limited to, peroxide-, silane-, sulfur-, radiation-, or azide-based cure systems. A full description of the various cross-linking technologies is  
30   described in copending U.S. Patent No's 5,869,591 and 5,977,271.

The crosslinking agent(s) will typically be provided in an amount to yield the desired degree of cross-linking, that is, 1 weight percent or greater, preferably 5 weight percent or greater and most preferably 10 weight percent or greater gel based upon the total weight of polymer or fabricated article, as measured according to ASTM D-2765-84, Method A.

The term "crosslinking agent" as used herein means a compound or mixture of compounds used for the purposes of coupling, grafting or crosslinking a polymer or polymer blend. The crosslinking agents used to prepare the compositions of the present invention include, but are not limited to peroxides, silanes, radiation, azides, phenols (as disclosed in USP 4,311,628), aldehyde-amine reaction products (including formaldehyde-ammonia; formaldehyde-ethylchloride-ammonia; acetaldehyde-ammonia; formaldehyde-aniline; butyraldehyde-aniline; and heptaldehyde-aniline), substituted ureas (include trimethylthiourea; diethylthiourea; dibutylthiourea; tripentylthiourea; 1,3-bis(2-benzothiazolylmercaptomethyl)urea; and N,N-diphenylthiourea), substituted guanidines (including diphenylguanidine; di-o-tolylguanidine; diphenylguanidine phthalate; and the di-o-tolylguanidine salt of dicatchol borate); substituted xanthates (including zinc ethylxanthate; sodium isopropylxanthate; butylxanthic disulfide; potassium isopropylxanthate; and zinc butylxanthate); substituted dithiocarbamates (including copper dimethyl-, zinc dimethyl-, tellurium diethyl-, cadmium dicyclohexyl-, lead dimethyl-, lead dimethyl-, selenium dibutyl-, zinc pentamethylene-, zinc didecyl-, and zinc isopropyl-octyl-dithiocarbamate); sulfur-containing compounds, such as thiazoles (including 2-mercaptobenzothiazole, zinc mercaptothiazolyl mercaptide, 2-benzothiazolyl-N,N-diethylthiocarbamyl sulfide, and 2,2'-dithiobis(benzothiazole), imidazoles (including 2-mercaptoimidazoline and 2-mercapto-4,4,6-trimethyldihydropyrimidine), sulfenamides (including N-t-butyl-2-benzothiazole-, N-cyclohexylbenzothiazole-, N,N-diisopropylbenzothiazole-, N-(2,6-dimethylmorpholino)-2-benzothiazole-, and N,N-diethylbenzothiazole-sulfenamide)thiuramidisulfides (including N,N'-diethyl-, tetrabutyl-, N,N'-diisopropyldioctyl-, tetramethyl-, N,N'-dicyclohexyl-, and N,N'-tetralauryl-thiuramidisulfide), paraquinonedioxime, dibenzoparaquinonedioxime, sulfur; and combinations thereof. See Encyclopedia of Chemical Technology, Vol. 17, 2nd edition, Interscience Publishers, 1968; also Organic Peroxides, Daniel Seern, Vol. 1, Wiley-Interscience, 1970),

The various crosslinking and coupling technologies are described in U.S. Patent No's 5,869,591 and 5,977,271. Dual cure systems, which use a combination of heat, moisture cure, and radiation steps, may be effectively employed. Dual cure systems are disclosed and claimed in U. S. Patent No. 6,124,370. For instance, it may be desirable to employ peroxide coupling agents in conjunction with silane coupling agents, peroxide coupling agents in conjunction with radiation, sulfur-containing coupling agents in conjunction with silane coupling agents, etc.

Suitable peroxides include aromatic diacyl peroxides; aliphatic diacyl peroxides; dibasic acid peroxides; ketone peroxides; alkyl peroxyesters; alkyl hydroperoxides (for example, diacetylperoxide; dibenzoylperoxide; bis-2,4-dichlorobenzoyl peroxide; di-tert-butyl peroxide; dicumylperoxide; tert-butylperbenzoate; tert-butylcumylperoxide; 2,5-bis (t-butylperoxy)-2,5-dimethylhexane; 2,5-bis (t-butylperoxy)-2,5-dimethylhexyne-3; 4,4,4',4'-tetra-(t-butylperoxy)-2,2-dicyclohexylpropane; 1,4-bis-(t-butylperoxyisopropyl)-benzene; 1,1-bis-(t-butylperoxy)-3,3,5-trimethylcyclohexane; lauroyl

peroxide; succinic acid peroxide; cyclohexanone peroxide; t-butyl peracetate; butyl hydroperoxide; etc. The preferred include 2,5-dimethyl-2,5-di-(t-butylperoxy) hexyne-3 and 2,5-dimethyl-2,5-di-(t-butylperoxy) hexane, the former is available as Lupersol™ 130 and the latter as Lupersol™ 101, both trademarks and products of Elf Atochem.

5           Suitable azide crosslinking agents include azidoformates, such as tetramethylenebis(azidoformate) (see, also, USP 3,284,421, Breslow, Nov. 8, 1966); aromatic polyazides, such as 4,4'-diphenylmethane diazide (see, also, USP 3,297,674, Breslow et al., Jan. 10, 1967); and the poly(sulfonyl azides), such as p,p'-oxybis-(benzene sulfonyl azide).

          The poly(sulfonyl azides) are any compounds having at least two sulfonyl azide groups (-SO<sub>2</sub>N<sub>3</sub>) reactive with the polymer(s). Preferably the poly(sulfonyl azide)s have a structure X-R-X wherein each X is SO<sub>2</sub>N<sub>3</sub> and R represents an unsubstituted or inertly substituted hydrocarbonyl, hydrocarbonyl ether or silicon-containing group, preferably having sufficient carbon, oxygen or silicon, preferably carbon, atoms to separate the sulfonyl azide groups sufficiently to permit a facile reaction between the polymer(s) and the sulfonyl azide, more preferably at least 1, more preferably at least 2, 15 most preferably at least 3 carbon, oxygen or silicon, preferably carbon, atoms between functional groups. While there is no critical limit to the length of R, each R advantageously has at least one carbon or silicon atom between X's and preferably has less than 50, more preferably less than 30, most preferably less than 20 carbon, oxygen or silicon atoms. Within these limits, larger is better for reasons including thermal and shock stability. When R is straight-chain alkyl hydrocarbon, there are 20 preferably less than 4 carbon atoms between the sulfonyl azide groups to reduce the propensity of the nitrene to bend back and react with itself. Silicon containing groups include silanes and siloxanes, preferably siloxanes. The term inertly substituted refers to substitution with atoms or groups which do not undesirably interfere with the desired reaction(s) or desired properties of the resulting coupled polymers. Such groups include fluorine, aliphatic or aromatic ether, siloxane as well as sulfonyl azide 25 groups when more than two polyolefin chains are to be joined. Suitable structures include R as aryl, alkyl, aryl alkaryl, arylalkyl silane, siloxane or heterocyclic, groups and other groups which are inert and separate the sulfonyl azide groups as described. More preferably R includes at least one aryl group between the sulfonyl groups, most preferably at least two aryl groups (such as when R is 4,4'-diphenylether or 4,4'-biphenyl). When R is one aryl group, it is preferred that the group have more 30 than one ring, as in the case of naphthylene bis(sulfonyl azides). Poly(sulfonyl)azides include such compounds as 1, 5-pentane bis(sulfonyl azide), 1,8-octane bis(sulfonyl azide), 1,10-decane bis(sulfonyl azide), 1,10-octadecane bis(sulfonyl azide), 1-octyl-2,4,6-benzene tris(sulfonyl azide), 4,4'-diphenyl ether bis(sulfonyl azide), 1,6-bis(4'-sulfonazidophenyl)hexane, 2,7-naphthalene bis(sulfonyl azide), and mixed sulfonyl azides of chlorinated aliphatic hydrocarbons containing an average of from 1 to 8 35 chlorine atoms and from 2 to 5 sulfonyl azide groups per molecule, and mixtures thereof. Preferred

poly(sulfonyl azide)s include oxy-bis(4-sulfonylazidobenzene), 2,7-naphthalene bis(sulfonyl azido), 4,4'-bis(sulfonyl azido)biphenyl, 4,4'-diphenyl ether bis(sulfonyl azide) and bis(4-sulfonyl azidophenyl)methane, and mixtures thereof.

Sulfonyl azides are conveniently prepared by the reaction of sodium azide with the  
5 corresponding sulfonyl chloride, although oxidation of sulfonyl hydrazines with various reagents (nitrous acid, dinitrogen tetroxide, nitrosonium tetrafluoroborate) has also been used.

Polyfunctional compounds capable of insertions into C-H bonds also include carbene-forming compounds such as salts of alkyl and aryl hydrazones and diazo compounds, and nitrene-forming compounds such as alkyl and aryl azides ( $R-N_3$ ), acyl azides ( $R-C(O)-N_3$ ), azidoformates ( $R-O-C(O)-N_3$ ), sulfonyl azides ( $R-SO_2-N_3$ ), phosphoryl azides ( $(RO)_2-(PO)-N_3$ ), phosphinic azides ( $R_2-P(O)-N_3$ ) and silyl azides ( $R_3-Si-N_3$ ).  
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Alternatively, silane crosslinking agents may be employed. In this regard, any silane that will effectively crosslink or couple the polymers of this invention can be used. Suitable silanes include unsaturated silanes that comprise an ethylenically unsaturated hydrocarbyl group, such as a vinyl,  
15 allyl, isopropenyl, butenyl, cyclohexenyl or  $\gamma$ -(meth)acryloxy allyl group, and a hydrolyzable group, such as, for example, a hydrocarbyloxy, hydrocarbonyloxy, or hydrocarbylamino group. Examples of hydrolyzable groups include methoxy, ethoxy, formyloxy, acetoxy, propionyloxy, and alkyl or arylamino groups. Preferred silanes are the unsaturated alkoxy silanes which can be grafted onto the polymer. These silanes and their method of preparation are more fully described in USP 5,266,627 to  
20 Meverden, et al. Vinyl trimethoxy silane (VTMOS), vinyl triethoxy silane,  $\gamma$ -(meth)acryloxy propyl trimethoxy silane and mixtures of these silanes are the preferred silane crosslinking agents for use in this invention.

The amount of silane crosslinking agent used in the practice of this invention can vary widely depending upon the nature of the substantially random interpolymer, the silane employed, the  
25 processing conditions, the amount of grafting initiator, the ultimate application, and similar factors.

The silane crosslinking agent is used to couple the polymers of this invention by any conventional method, typically in the presence of a free radical initiator for example peroxides and azo compounds, or by ionizing radiation, etc. Organic initiators are preferred, such as any one of the peroxide initiators, for example, dicumyl peroxide, di-tert-butyl peroxide, t-butyl perbenzoate,  
30 benzoyl peroxide, cumene hydroperoxide, t-butyl peroctoate, methyl ethyl ketone peroxide, 2,5-dimethyl-2,5-di(t-butyl peroxy)hexane, lauryl peroxide, and tert-butyl peracetate. A suitable azo compound is azobisisobutyl nitrite.

Those skilled in the art will be readily able to select amounts of initiator employed, with the amount selected taking into account characteristics of the polymers, such as molecular weight, molecular weight distribution, comonomer content, as well as the presence of coupling enhancing coagents, additives (such as oil) etc. Typically, the amount of initiator employed will not exceed that which is required to effect crosslinking.

While any conventional method can be used to silane graft the polymers, one preferred method is blending the two with the initiator in the first stage of a reactor extruder, such as a Buss kneader. The grafting conditions can vary, but the melt temperatures are typically between 160°C and 260°C, preferably between 190°C and 230°C, depending upon the residence time and the half-life of the initiator.

Cure is promoted with a coupling catalyst, and any catalyst that will provide this function can be used in this invention. These catalysts generally include organic bases, carboxylic acids, and organometallic compounds including organic titanates and complexes or carboxylates of lead, cobalt, iron, nickel, zinc and tin. Dibutyltindilaurate, dioctyltinmaleate, dibutyltindiacetate, dibutyltindioctoate, stannous acetate, stannous octoate, lead naphthenate, zinc caprylate, cobalt naphthenate. Tin carboxylate, especially dibutyltindilaurate and dioctyltinmaleate, are particularly effective for this invention.

Rather than employing a chemical crosslinking agent, crosslinking may be effected by use of radiation. Useful radiation types include electron beam or beta ray, gamma rays, X-rays, or neutron rays. Radiation is believed to effect crosslinking by generating polymer radicals which may combine and crosslink. Additional teachings concerning radiation coupling are seen in C. P. Park, "Polyolefin Foam" Chapter 9, Handbook of Polymer Foams and Technology, D. Klemperer and K. C. Frisch, eds., Hanser Publishers, New York (1991), pages 198 - 204.

Radiation dosage depends upon the blend polymer compositions. Those skilled in the art will be readily able to select suitable radiation levels, taking into account such variables as thickness and geometry of the article to be irradiated, as well as to characteristics of the polymers, such as molecular weight, molecular weight distribution, comonomer content, the presence of coupling enhancing coagents, additives (such as oil), etc. Typically, the dosage will not exceed that which is required to effect the desired level of crosslinking.

The choice of crosslinking agent will depend on the types of polymers being crosslinked. The crosslinking agent may be added in a variety of ways. For instance, powder or liquid or pellets may be added to and/or tumble blended with one or more of the blend polymer components which have preferably (but not necessarily) been surface treated with

tackifiers. Tackifiers can be obtained by the polymerization of petroleum and terpene feedstreams and from the derivatization of wood, gum, and tall oil rosin. Several classes of tackifiers include wood rosin, tall oil and tall oil derivatives, and cyclopentadiene derivatives, such as are described in United Kingdom patent application GB 2,032,439A. Other classes of tackifiers include aliphatic C<sub>5</sub> resins, polyterpene resins, hydrogenated resins, mixed aliphatic-aromatic resins, rosin esters, natural and synthetic terpenes, terpene-phenolics, and hydrogenated rosin esters. A preferred tackifier is mineral oil.

Alternatively, the crosslinking agent is dispersed in a suitable non-reactive liquid or tackifier (such as mineral oil) which is then tumble blended with one or more of the blend polymer components. It is especially preferred that the oil is of a room temperature viscosity such that it has sufficient flow to completely wet the surface of the pellets, and yet be sufficiently viscous such it does not drain quickly on standing prior to feeding to the extruder. A preferred oil is mineral oil. The dispersion of crosslinking agent in non-reactive liquid may also be injected into a melt processing equipment (such as an extruder) used to make the blend compositions.

The amount of non-reactive liquid or tackifier (such as mineral oil) used will vary, and typically is in the range of 0.2-2.0 wt percent (but this is not limiting). Alternatively, the crosslinking agent may first be compounded in a suitable thermoplastic polymer and pellets, etc of the compound may then be tumble blended with the other blend components before reactive extrusion or independently fed to the extruder.

Those skilled in the art will be readily able to select amounts of crosslinking agent, with the amount selected taking into account characteristics of the polymer(s) such as molecular weight, molecular weight distribution, comonomer content, the presence of crosslinking enhancing coagents, additives (such as oil) etc. Since it is contemplated that the polymer(s) may be blended prior to crosslinking, those skilled in the art may use the following guidelines as a reference point in optimizing the amount of crosslinking agent preferred for the particular blends in question. Typically, the amount of crosslinking agent employed will not exceed that which is required to effect the desired level of crosslinking.

Treatment of blends with the crosslinking agent according to the practice of the invention results in blends of the invention, which are referred to herein as crosslinked or coupled or grafted blends. A blend is advantageously mixed with a crosslinking agent above the softening temperature of at least one component of the blend, most preferably below the peak decomposition temperature of the crosslinking agent, and the resulting mixture is preferably raised to at least the peak decomposition temperature of the crosslinking agent.

The crosslinking agent and polymer composition are mixed at a first temperature which is at least the melting point of the lowest melting component of the blend and, after mixing, are heated to react at a second temperature which is at least greater than the first temperature and is usually greater than 100°C and most frequently greater than 150°C. The preferred temperature range depends on the nature of the crosslinking agent that is used. For example, in the case of azides (including but not limited to 4,4'-disulfonylazidediphenylether) and peroxides (including but not limited to 2,5-bis (t-butylperoxy)-2,5-dimethylhexyne-3), the preferred temperature range is greater than 150°C, preferably greater than 160°C, more preferably greater than 185°C, most preferably greater than 190°C. Preferably, the upper temperature is less than 300°C.

Temperatures for use in the practice of the invention are also determined by the softening or melt temperatures of the polymer starting materials. For these reasons, the temperature is advantageously greater than 90°C, preferably greater than 120°C, more preferably greater than 150°C, and most preferably greater than 170°C.

In some cases, further improvements in crosslinking may be achieved by reacting at temperatures greater than or equal to 240°C, more preferably greater than or equal to 250°C even more preferably greater than or equal to 260°C.

Preferred times at the desired decomposition temperatures are times that are sufficient to result in complete reaction of the crosslinking agent with the polymer(s). Preferred reaction times in terms of the half-life of the crosslinking agent (that is the time required for about half of the agent to be reacted at a preselected temperature, and determinable by DSC) is about 5 half-lives of the crosslinking agent. In the case of a bis(sulfonyl azide), for instance, the reaction time is preferably at least about 4 minutes at 200°C.

Admixing of the polymer and crosslinking agent is conveniently accomplished by any means within the skill in the art. Desired distribution is different in many cases, depending on what properties are to be modified. In a blend it is often desirable to have low solubility in one or more of the polymer matrices such that the crosslinking agent is preferentially in the other phase, or predominantly in the interfacial region between the two phases.

Practice of the invention advantageously involves forming a substantially uniform admixture of polymers and crosslinking agent (before its decomposition). In the case of blends where there are dispersed and continuous phases, it may be sufficient for the crosslinking agent to be dispersed at the interface of the phases rather than being uniformly distributed.

Processes for crosslinking include at least one of (a) dry blending the coupling agent with the polymer, preferably to form a substantially uniform admixture and adding this mixture to melt processing equipment, for example, a melt extruder to achieve the crosslinking reaction, at a temperature at least the decomposition temperature of the crosslinking agent; (b) introducing, for

example, by injection, a crosslinking agent in liquid form, for example, dissolved in a solvent therefor or in a slurry of crosslinking agent in a liquid, into a device containing polymer, preferably softened, molten or melted polymer, but alternatively in particulate form, in solution or dispersion, more preferably in melt processing equipment; (c) forming a first admixture of a first amount of a first polymer and a crosslinking agent, advantageously at a temperature less than about the decomposition temperature of the crosslinking agent, preferably by melt blending, and then forming a second admixture of the first admixture with a second amount of a second polymer (for example a concentrate of a crosslinking agent admixed with at least one polymer and optionally other additives, is conveniently admixed into a second polymer or combination thereof optionally with other additives, to modify the second polymer(s)); (d) feeding at least one crosslinking agent, preferably in solid form, more preferably finely comminuted, for example, powder, directly into softened or molten polymer, for example, in melt processing equipment, for example, in an extruder; or combinations thereof.

Process (c) is conveniently used to make a concentrate with a first polymer composition having a lower melting temperature, advantageously at a temperature below the decomposition temperature of the crosslinking agent, and the concentrate is melt blended into a second polymer composition having a higher melting temperature to complete the crosslinking reaction.

Concentrates are especially preferred when temperatures are sufficiently high to result in loss of crosslinking agent by evaporation or decomposition not leading to reaction with the polymer, or other conditions would effect that result. Alternatively, some crosslinking occurs during the blending of the first polymer and crosslinking agent, but some of the crosslinking agent remains unreacted until the concentrate is blended into the second polymer composition. The polymer composition optionally includes additives known within the skill in the art. When the crosslinking agent is added in a dry form it is preferred to mix the agent and polymer in a softened or molten state below the decomposition temperature of the crosslinking agent, then to heat the resulting admixture to a temperature at least equal to the decomposition temperature of the crosslinking agent.

The polymers and crosslinking agent are suitably combined in any manner which results in desired reaction thereof, preferably by mixing the crosslinking agent with the polymer(s) under conditions which allow sufficient mixing before reaction to avoid uneven amounts of localized reaction then subjecting the resulting admixture to heat sufficient for reaction. Preferably, a substantially uniform admixture of crosslinking agent and polymer is formed before exposure to conditions in which chain coupling takes place.

A substantially uniform admixture is one in which the distribution of crosslinking agent in the polymer is sufficiently homogeneous to be evidenced by a polymer having a melt viscosity after treatment according to the practice of the invention either higher at low angular frequency (for



example, 0.1 rad/sec) or lower at higher angular frequency (for example, 100 rad/sec) than that of the same polymer which has not been treated with the crosslinking agent but has been subjected to the same shear and thermal history.

Thus, preferably, in the practice of the invention, decomposition of the crosslinking agent occurs after mixing sufficient to result in a substantially uniform admixture of crosslinking agent and polymer. This mixing is preferably attained with the polymer in a molten or melted state, which is above the crystalline melt temperature, or in a dissolved or finely dispersed condition rather than in a solid mass or particulate form. The molten or melted form is more preferred to insure homogeneity rather than localized concentrations at the surface.

While any equipment can be suitably used, equipment which provides sufficient mixing and temperature control in the same equipment, including such devices as an extruder, or a static polymer mixing device such as a Brabender blender, are preferred. The term extruder is used in its broadest meaning to include such devices as those, which extrude pellets such as a pelletizer.

For polymers that have softening points above the crosslinking agent decomposition temperature (preferably greater than 200°C), and especially when incorporation of a lower melting polymer (such as in a concentrate) is undesirable, the preferred method for incorporation of crosslinking agent is to solution blend the crosslinking agent in solution or admixture into the polymer, (this allows the polymer to imbibe that is absorb or adsorb at least some of the coupling agent), and then to evaporate the solvent. After evaporation, the resulting mixture is extruded. The solvent is preferably a solvent for the crosslinking agent, and more preferably also for the polymer when the polymer is soluble such as in the case of polycarbonate. Such solvents include polar solvents such as acetone, THF (tetrahydrofuran) and chlorinated hydrocarbons such as methylene chloride. Alternatively other non-polar compounds such as mineral oils in which the crosslinking agent is sufficiently miscible to disperse the crosslinking agent in a polymer, are used.

Applications which can utilize the above filled polymer compositions comprising the crosslinkable substantially random interpolymers and optionally one or more thermoplastics (which also may be uncrosslinked or crosslinked) include, but are not limited to, power distribution systems, such as wire and cable, construction materials such as flooring systems, sound and vibration management systems, toys, sporting goods, appliances, automotive interiors (trim, mats, insulation), automotive exteriors, automotive under the hood, lawn and garden, personal protective wear, apparel, foot wear, traffic cones, housewares, films, multilayer films, sheets, barrier membranes, protective coatings, coated fabrics, medical tubing and hoses, industrial tubing and hoses, profile extrusions, seals and gaskets, medical, handles and grips. upholstery, industrial covers, luggage, artificial leather goods, and tapes.

The polymer compositions described above may be converted to foam products using any conventional process. Foam products include, for example, extruded thermoplastic polymer foam, extruded polymer strand foam, expandable thermoplastic foam beads, expanded thermoplastic foam beads or expanded and fused thermoplastic foam beads, and various types of crosslinked foams. The foam products may take any known physical configuration, such as sheet, round, strand geometry, rod, film, solid plank, laminated plank, coalesced strand plank, profiles and bun stock. The foam products may be converted into fabricated articles using any conventional process or method. For example, any one or more of expansion, coalescing and welding may be used in making such articles, especially from expandable foam beads. One may also mold expandable beads into any known configuration that employs foam products, including, but not limited to the foregoing configurations.

Foam forming steps of the process are known in the art. For instance as exemplified by the teachings to processes for making ethylenic polymer foam structures and processing them in C. P. Park. "Polyolefin Foam", Chapter 9, Handbook of Polymer Foams and Technology, edited by D. Klempner and K. C. Frisch, Hanser Publishers, Munich, Vienna, New York, Barcelona (1991).

In one embodiment of the invention, the crosslinking process takes place in a single vessel, that is mixing of the crosslinking agent and polymer takes place in the same vessel as heating to the decomposition temperature of the crosslinking agent. The vessel is preferably an extruder, which may optionally be suitable for foam preparation. The reaction vessel more preferably has at least two zones of different temperatures into which a reaction mixture passes. The first zone advantageously is at a temperature of at least the crystalline melt temperature or the softening temperature of the polymer(s) and preferably less than the decomposition temperature of the crosslinking agents, with the second zone being at a temperature sufficient for decomposition of the crosslinking agent. The first zone is preferably at a temperature sufficiently high to soften the polymer and allow it to combine with the crosslinking agent, through distributive mixing to a substantially uniform admixture. Addition of a blowing agent may optionally occur in either of these zones, depending on the temperatures advantageous for its use.

In one embodiment the foam forming step or steps and the coupling steps are at least partially simultaneous. Thus the crosslinking agent is introduced during any step before or in a foam forming process that is of a temperature sufficiently low to result in adequate mixing before or during grafting and grafting takes place in or simultaneous with any step in a foam forming process in which the temperature is at least about the decomposition temperature of the crosslinking agent. Crosslinking, however, preferably takes place before the foam is extruded or otherwise exits the vessel in which the polymer is admixed with any blowing agent.

Foams of the present invention may be substantially noncrosslinked. That is, the foam structure contains 1 to 30 weight percent, preferably 1 to 20 weight percent, more preferably 1 to 10

weight percent gel based upon the total weight of foam or polymer, as measured according to ASTM D-2765-84, Method A.

Alternatively, the polymer compositions could be used to make foams which are substantially cross-linked (that is, contain greater than 30 weight percent gel based upon the total weight of foam or polymer, as measured according to ASTM D-2765-84 Method A) by addition of any known cross-linking agent. The various crosslinking agents and technologies are described in the art. Cross-linking may be induced by addition of a cross-linking agent. Induction of cross-linking and exposure to an elevated temperature to effect foaming or expansion may occur simultaneously or sequentially. If a chemical cross-linking agent is used, it is incorporated into the polymer material in the same manner as the chemical blowing agent. Further, if a chemical cross-linking agent is used, the foamable melt polymer material is heated or exposed to a temperature of preferably less than 150°C to prevent decomposition of the cross-linking agent or the blowing agent and to prevent premature cross-linking. If radiation cross-linking is used, the foamable melt polymer material is heated or exposed to a temperature of preferably less than 160°C to prevent decomposition of the blowing agent. The foamable melt polymer material is extruded or conveyed through a die of desired shape to form a foamable structure. The foamable structure is then cross-linked and expanded at an elevated or high temperature (typically, 150°C-250°C) such as in an oven to form a foam structure. If radiation cross-linking is used, the foamable structure is irradiated to cross-link the polymer material, which is then expanded at the elevated temperature as described above. The present structure can advantageously be made in sheet or thin plank form according to the above process using either cross-linking agents or radiation.

The present crosslinked foam structure may also be made into a continuous plank structure by an extrusion process utilizing a long-land die as described in GB 2,145,961A. In that process, the polymer, chemical blowing agent and cross-linking agent are mixed in an extruder, heating the mixture to let the polymer cross-link and the blowing agent to decompose in a long-land die; and shaping and conducting away from the foam structure through the die with the foam structure and the die contact lubricated by a proper lubrication material.

The present crosslinked foam structure may be made in bun stock form by two different processes. One process involves the use of a cross-linking agent and the other uses radiation.

The present crosslinked foam structure may be made in bun stock form by mixing the blends of this invention, a cross-linking agent, and a chemical blowing agent to form a slab, heating the mixture in a mold so the cross-linking agent can cross-link the polymer material and the blowing agent can decompose, and expanding by release of pressure in the mold. Optionally, the bun stock formed upon release of pressure may be re-heated to effect further expansion.

Foam may be made from cross-linked polymer sheet by either irradiating polymer sheet with high energy beam or by heating a polymer sheet containing chemical cross-linking agent. The cross-linked polymer sheet is cut into the desired shapes and impregnated with nitrogen in a higher pressure at a temperature above the softening point of the polymer; releasing the pressure effects nucleation of bubbles and some expansion in the sheet. The sheet is re-heated at a lower pressure above the softening point, and the pressure is then released to allow foam expansion.

The foam structures of the present invention are optionally made by a conventional extrusion foaming process. The structure is advantageously prepared by heating the polymer or blend to form a plasticized or melt polymer material, incorporating therein a blowing agent to form a foamable gel, and extruding the gel through a die to form the foam product. Depending upon the die (with an appropriate number of apertures) and operating conditions, the product may vary from an extruded foam plank or rod through a coalesced foam strand product, to foam beads and eventually to chopped strands of foamable beads. Prior to mixing with the blowing agent, the polymer material is heated to a temperature at or above its glass transition temperature or melting point. The blowing agent is optionally incorporated or mixed into the melt polymer material by any means known in the art such as with an extruder, mixer, blender, or the like. The blowing agent is mixed with the melt polymer material at an elevated pressure sufficient to prevent substantial expansion of the melt polymer material and to advantageously disperse the blowing agent homogeneously therein. Optionally, a nucleator is optionally blended in the polymer melt or dry blended with the polymer material prior to plasticizing or melting. Prior to extruding foamable gel through the die, one typically cools the gel to an optimum temperature. The foamable gel is typically cooled to a lower temperature to optimize physical characteristics of the foam structure. This temperature, often referred to as the foaming temperature, is typically above each component's polymer glass transition temperature ( $T_g$ ), or for those having sufficient crystallinity, near the peak crystalline melting temperature ( $T_m$ ). "Near" means at, above, or below and largely depends upon where stable foam exists. The temperature desirably falls within 30° centigrade (°C) above or below the  $T_m$ . For foams of the present invention, an optimum foaming temperature is in a range in which the foam does not collapse. The gel may be cooled in the extruder or other mixing device or in separate coolers. The gel is then extruded or conveyed through a die of desired shape to a zone of reduced or lower pressure to form the foam structure. The zone of lower pressure is at a pressure lower than that in which the foamable gel is maintained prior to extrusion through the die. The lower pressure is optionally superatmospheric or subatmospheric (vacuum), but is preferably at an atmospheric level.

In another embodiment, the resulting foam structure is optionally formed in a coalesced strand form by extrusion of the polymer material through a multi-orifice die. The orifices are arranged so that contact between adjacent streams of the molten extrudate occurs during the foaming

process and the contacting surfaces adhere to one another with sufficient adhesion to result in a unitary foam structure. The streams of molten extrudate exiting the die take the form of strands or profiles, which desirably foam, coalesce, and adhere to one another to form a unitary structure. Desirably, the coalesced individual strands or profiles should remain adhered in a unitary structure to prevent strand delamination under stresses encountered in preparing, shaping, and using the foam. Apparatuses and method for producing foam structures in coalesced strand form are seen in U.S. Pat. Nos. 3,573,152 and 4,824,720.

Alternatively, the resulting foam structure is conveniently formed by an accumulating extrusion process and apparatus as seen in U.S. Pat. No. 4,323,528 and USP 5,817,705. This apparatus, commonly known as an "extruder-accumulator system" allows one to operate a process on an intermittent, rather than a continuous, basis. The apparatus includes a holding zone or accumulator where foamable gel remains under conditions that preclude foaming. The holding zone is equipped with an outlet die that opens into a zone of lower pressure, such as the atmosphere. The die has an orifice that may be open or closed, preferably by way of a gate that is external to the holding zone. Operation of the gate does not affect the foamable composition other than to allow it to flow through the die. Opening the gate and substantially concurrently applying mechanical pressure on the gel by a mechanism (for example, a mechanical ram) forces the gel through the die into a zone of lower pressure. The mechanical pressure is sufficient to force foamable gel through the die at a rate fast enough to preclude significant foaming within the die yet slow enough to minimize and preferably eliminate generation of irregularities in foam cross-sectional area or shape. As such, other than operating intermittently, the process and its resulting products closely resemble those made in a continuous extrusion process.

In the accumulating extrusion process, low density foam structures having large lateral cross-sectional areas are prepared by: 1) forming under pressure a gel of the polymer or blend material and a blowing agent at a temperature at which the viscosity of the gel is sufficient to retain the blowing agent when the gel is allowed to expand; 2) extruding the gel into a holding zone maintained at a temperature and pressure which does not allow the gel to foam, the holding zone having an outlet die defining an orifice opening into a zone of lower pressure at which the gel foams, and an openable gate closing the die orifice; 3) periodically opening the gate; 4) substantially concurrently applying mechanical pressure by a movable ram on the gel to eject it from the holding zone through the die orifice into the zone of lower pressure, at a rate greater than that at which substantial foaming in the die orifice occurs and less than that at which substantial irregularities in cross-sectional area or shape occurs; and 5) permitting the ejected gel to expand unrestrained in at least one dimension to produce the foam structure.

The present foam structures may also be formed into foam beads suitable for molding into articles by expansion of pre-expanded beads containing a blowing agent. The beads may be molded at the time of expansion to form articles of various shapes. Processes for making expanded beads and molded expanded beam foam articles are described in Plastic Foams, Part II, Frisch and Saunders, pp. 544-585, Marcel Dekker, Inc. (1973) and Plastic Materials, Brydson, 5th ed., pp. 426-429, Butterworths (1989). Expandable and expanded beads can be made by a batch or by an extrusion process, and may be substantially non-crosslinked or substantially crosslinked.

The batch process of making expandable beads is similar to manufacturing expandable polystyrene. The resulting foam structure is formed into non-crosslinked foam beads suitable for molding into articles. Discrete resin particles, such as granules made from the blends of the present invention, made either by melt blending or in-reactor blending, are impregnated with a blowing agent (and optionally a cross-linking agent) in an aqueous suspension or in an anhydrous state in a pressure vessel at an elevated temperature and pressure. In the case of the aqueous suspension, the blowing agent (and, optionally, cross-linking agent) is/are introduced into the liquid medium in which the granules are substantially insoluble (such as water) at an elevated pressure and temperature in an autoclave or other pressure vessel. The granules are either discharged rapidly into an atmosphere or a region of reduced pressure to expand the granules into foam beads or cooled and discharged as unexpanded beads. In a separate step, the unexpanded beads are heated to expand them, for example, with steam or with hot air. This process for making bead foams is well taught in U.S. Pat. Nos. 4,379,859 and 4,464,484.

In a modification of the bead process, styrene monomer is optionally impregnated into the suspended pellets of the blend compositions of the present invention prior to their impregnation with blowing agent to form a graft interpolymer with the polymer material. The resulting interpolymer beads are cooled and discharged from the vessel substantially unexpanded. The beads are then expanded and molded by an expanded polystyrene bead molding process within the skill in the art. Such a process of making such polyethylene/polystyrene interpolymer beads is described for instance in U.S. Pat. No. 4,168,353.

A variation of the foregoing extrusion process readily yields expandable thermoplastic polymer beads. The method tracks with the conventional foam extrusion process described above up to the die orifice, which now contains one or multiple holes. The variation requires (a) cooling the foamable gel to a temperature below that at which foaming occurs, (b) extruding cooled gel through a die containing one or more orifices to form a corresponding number of essentially continuous expandable thermoplastic strands, (c) optionally quenching the strands exiting the die orifice in a cold water bath; and (d) and pelletizing the expandable thermoplastic strands to form expandable

thermoplastic beads. Alternatively, the strands are converted to foam beads by cutting the strands into pellets or granules at the die face and allowing the granules to expand.

The foam beads can also be prepared by preparing a mixture of the polymer blend compositions of the present invention, cross-linking agent, and chemical blowing agent in a suitable mixing device or extruder and form the mixture into pellets, and heat the pellets to cross-link and expand.

In another process for making cross-linked foam beads suitable for molding into articles, the blends of this invention are melted and mixed with a physical blowing agent in a conventional foam extrusion apparatus to form an essentially continuous foam strand. The foam strand is granulated or pelletized to form foam beads. The foam beads are then cross-linked by radiation. The cross-linked foam beads may then be coalesced and molded to form various articles as described above for the other foam bead process. Additional teachings to this process are seen in U.S. Patent No. 3,616,365 and C.P. Park, supra, pp. 224-228.

The foam beads may then be molded by any means known in the art, such as charging the foam beads to the mold, compressing the mold to compress the beads, and heating the beads such as with steam to effect coalescing and welding of the beads to form the article. Optionally, the beads may be impregnated with air or other blowing agent at an elevated pressure and temperature prior to charging to the mold. Further, the beads may optionally be heated prior to charging. The foam beads are conveniently then molded to blocks or shaped articles by a suitable molding method known in the art. Some of the methods are taught in U.S. Pat. Nos. 3,504,068 and 3,953,558. Excellent teachings of the above processes and molding methods are seen in C.P. Park, supra, p. 191, pp. 197-198, and pp. 227-233, U. S. Patent Nos. 3,886,100, U. S. Patent Nos. 3,959,189, U. S. Patent Nos. 4,168,353 and U. S. Patent Nos. 4,429,059.

Blowing agents useful in making the foam structures of the present invention include inorganic agents, organic blowing agents and chemical blowing agents. Suitable inorganic blowing agents include carbon dioxide, nitrogen, argon, water, air, sulfur hexafluoride (SF<sub>6</sub>) and helium. Organic blowing agents include aliphatic hydrocarbons having 1-9 carbon atoms, aliphatic alcohols having 1-3 carbon atoms, and fully and partially halogenated aliphatic hydrocarbons having 1-4 carbon atoms. Aliphatic hydrocarbons include methane, ethane, propane, n-butane, isobutane, n-pentane, isopentane, neopentane. Aliphatic alcohols include methanol, ethanol, n-propanol, and isopropanol. Fully and partially halogenated aliphatic hydrocarbons include fluorocarbons, chlorocarbons, and chlorofluorocarbons. Examples of fluorocarbons include methyl fluoride, perfluoromethane, ethyl fluoride, 1,1-difluoroethane (HFC-152a), fluoroethane (HFC-161), 1,1,1-trifluoroethane (HFC-143a), 1,1,1,2-tetrafluoroethane (HFC-134a), 1,1,2,2-tetrafluoroethane (HFC-

134), 1,1,1,3,3-pentafluoropropane, pentafluoroethane (HFC-125), difluoromethane (HFC-32), perfluoroethane, 2,2-difluoropropane, 1,1,1-trifluoropropane, perfluoropropane, dichloropropane, difluoropropane, perfluorobutane, perfluorocyclobutane. Partially halogenated chlorocarbons and chlorofluorocarbons for use in this invention include methyl chloride, methylene chloride, ethyl chloride, 1,1,1-trichloroethane, 1,1-dichloro-1 fluoroethane (HCFC-141b), 1-chloro-1,1-difluoroethane (HCFC-142b), chlorodifluoromethane (HCFC-22), 1,1-dichloro-2,2,2-trifluoroethane (HCFC-123) and 1-chloro-1,2,2,2-tetrafluoroethane (HCFC-124). Fully halogenated chlorofluorocarbons include trichloromonofluoromethane (CFC-11), dichlorodifluoromethane (CFC-12), trichlorotrifluoroethane (CFC-113), dichlorotetrafluoroethane (CFC-114), chloroheptafluoropropane, and dichlorohexafluoropropane. Chemical blowing agents include azodicarbonamide, azodiisobutyro-nitrile, barium azodicarboxylate, N,N'-dimethyl-N,N'-dinitrosoterephthalamide, and benzenesulfonhydrazide, 4,4-oxybenzene sulfonyl semicarbazide, and p-toluene sulfonyl semicarbazide, trihydrazino triazine and mixtures of citric acid and sodium bicarbonate such as the various products sold under the name Hydrocerol™ (a product of Boehringer Ingelheim). Any of the foregoing blowing agents may be used singly or in combination with one or more other blowing agents. The amount of blowing agent incorporated into the polymer melt material to make a foam-forming polymer gel is from 0.05 to 5.0, preferably from 0.2 to 3.0, and most preferably from 0.5 to 2.5 gram moles per kilogram of polymer.

Foams are optionally perforated to enhance or accelerate gaseous permeation exchange wherein blowing agent exits from the foam and air enters into the foam. The resulting perforated foams have defined therein a multiplicity of channels that are preferably free of direction with respect to the longitudinal extension of the foam. The channels extend from one foam surface at least partially through the foam, and sometimes completely through the foam from one external surface to another external surface. The channels are advantageously present over substantially an entire exterior foam surface, preferably with uniform or substantially uniform spacing. Suitable spacing intervals may be up to and including 2.5 centimeters (cm), preferably up to and including 1.3 cm. The foams optionally employ a stability control agent of the type described above in combination with perforation to allow accelerated permeation or release of blowing agent while maintaining a dimensionally stable foam. U.S. Patents No. 5,424,016, . U.S. Patents No. 5,585,058, WO 92/19439 and WO 97/22455, provide excellent information relative to perforation. If desired, the foams of this invention may be post-treated by any known means to increase foam open cell content. Such post-treatment methods include, without limit, mechanically compressing the foam and expanding the foam by exposure to steam and/or hot air.

Foams of the present invention generally have a density less than 900, preferably less than 850, more preferably less than 800 kilograms per cubic meter, even more preferably from 5 to 700



kilograms per cubic meter, and most preferably from 5 to 200 kilograms per cubic meter (in accordance with ASTM D3575-93, Suffix W, Method B). The foams may be microcellular (i.e., with a cell size from less than 0.05 mm, preferably from 0.001 mm, to 0.05 mm) or macrocellular (that is, cell size of 0.05 mm or more). The macrocellular foam has an average cell size of 0.05 to 15, preferably from 0.1 to 10.0, and more preferably from 0.1 to 5 millimeters, preferably from 0.2 to 3 millimeters, and more preferably 0.2 to 2 millimeters as measured according to the procedures of ASTM D3576-77. The preferred ranges of density and cell size should not be taken as limiting the scope of this invention.

Foams of the present invention preferably exhibit excellent dimensional stability. Preferred foams retain 80 or more percent of their initial volume when measured one month after an initial volume measurement within 30 seconds after foam expansion. Volume is measured by any suitable method such as cubic displacement of water.

The foams of the present invention have an open cell content that ranges from 0 to 100 volume percent based on the total volume of foam, as measured according to ASTM D2856-94, depending upon component selection and process condition variations. Foams with an open cell content of 30 vol percent or less generally fall in a class known as closed cell foams. Those known as open cell foams typically have an open cell content greater than 30, preferably greater than 40, and more preferably greater than 50 vol percent. The open cell content is desirably 100 vol percent or less, preferably 95 vol percent or less, and more preferably 90 vol percent or less.

The foams of density less than  $100 \text{ kg/m}^3$  generally have an Asker-C hardness of  $< 90$ , desirably  $< 80$ , and preferably  $< 70$ . Hardness measurements of the foams use an Asker C durometer for cellular rubber and yarn in accordance with ASTM D2240-97, using a 5 mm diameter spherical indenter.

If the foam is in the shape of a sheet or plank, it has a thickness that is generally  $> 0.5 \text{ mm}$ , preferably  $> 1 \text{ mm}$  and a width that is generally  $> 5 \text{ mm}$ , preferably  $> 10 \text{ mm}$ . As used herein "thickness" of a foam plank or sheet refers to its smallest cross-sectional dimension (for example, as measured from one planar surface to an opposing planar surface). When the foam is present as a round or rod, it has a diameter that is generally  $> 5 \text{ mm}$ , preferably  $> 10 \text{ mm}$ .

In another aspect, the polymer compositions of this invention may be used to make foamed films. The film of the present invention may be a monolayer or a multilayer film. One or more layers of the film may be oriented or foamed. A multi-layer film of the present invention may contain one, two or more layers comprising a blend as defined herein. In one embodiment, the film according to the invention has a thickness of 0.5 to 100 mils. Preferably, the present invention pertains to a tough and stiff film, comprising the blends of this invention. The film of the invention may be printed. The

film of the invention is obtainable according to methods known in the art. The film may be made using a blown or a cast film extrusion process, including co-extrusion and extrusion coating. One or more layers of the film may be expanded, for example with a conventional blowing agent, to make foamed film. One or more films may be laminated to form a multi-layer structure. Preferred are two-  
5 layer or three-layer films with one or two surface layers and the foamed layer being the core layer. The surface layers may or may not comprise the blends of this invention. In a three layer structure, preferably, the foamed layer is the core or middle layer. The films may be (further) oriented after forming via tenter frame, double-bubble or other blown film techniques.

Foamed film is especially suitable for use as label or in thermoformable articles of  
10 manufacture. To make foamed film structures, either physical or chemical blowing agents may be used. A multilayer film of the invention comprising one or more foamed layers comprising the polymer compositions as defined herein is obtainable according to methods known in the art, for example, using a co-extrusion process.

The label film may be constructed from printed, slit to width, rolls of film with the labels  
15 glued to a container, for example a bottle, using conventional adhesives and glues known to the industry. In addition, the films of this invention may be printed, coated with pressure sensitive adhesives, laminated to release papers or films and applied to bottles, containers or other surfaces by conventional pressure sensitive techniques. The bottle may be a glass bottle or a PET bottle. Covering or affixed to a glass bottle, the label may also serve a protective purpose. If the bottle is a PET bottle,  
20 the preferred label is a wrap-around label.

The foams, films and other fabricated articles of the present invention may be used in applications including, without limit, cushion packaging (for example, corner blocks, braces, saddles, pouches, bags, envelopes, overwraps, interleaving, encapsulation) of finished electronic goods such as computers, televisions, and kitchen appliances; packaging or protection of explosive materials or  
25 devices; material handling (trays, tote boxes, box liners, tote box inserts and dividers, shunt, stuffing, boards, parts spacers and parts separators); work station accessories (aprons, table and bench top covers, floor mats, seat cushions); automotive (headliners, impact absorption in bumpers or doors, carpet underlayment, sound insulation); flotation (for example, life jackets, vests and belts); sports and leisure or athletic and recreational products (for example, gym mats and bodyboards); egg  
30 cartons, meat trays, fruit trays, thermal insulation (such as that used in building and construction for wall sheathing, roofing, foundation insulation and residing underlayment); acoustical insulation (for example, for appliances and building and construction); pipe insulation, insulation for refrigeration, buoyancy applications (for example, floatintg docks and rafts), floral and craft products, pallets, luggage liners, desk pads, footwear (including shoe soles), insulation blankets for greenhouses, case

inserts, display foams, gaskets, grommets, seals; sound attenuation for printers and typewriters; display case insert; missile container padding; military shell holder; blocking and bracing of various items in transport; preservation and packaging; automotives anti-rattle pads, seals; medical devices, skin contact pads; cushioned pallet; and vibration isolation pad. The foregoing list merely illustrates a number of suitable applications. Skilled artisans can readily envision additional applications without departing from the scope or spirit of the present invention.

The foregoing list merely illustrates a number of suitable applications. Skilled artisans can readily envision additional applications without departing from the scope or spirit of the present invention.

Various additives may optionally be incorporated into the compositions or fabricated articles of the present invention. The additives include, without limitation, stability control agents, nucleating agents, inorganic fillers, conductive fillers, pigments, colorants, antioxidants, acid scavengers, ultraviolet absorbers or stabilizers, flame retardants, processing aids, extrusion aids, anti-static agents, cling additives (for example, polyiso-butylene), antiblock additives, other thermoplastic polymers.

Certain of the additives, such as inorganic and conductive fillers, may also function as nucleating agents and/or open cell promoters for foams. Examples of antioxidants are hindered phenols (such as, for example, Irganox™ 1010) and phosphites (for example, Irgafos™ 168) both trademarks of, and commercially available from, Ciba Geigy Corporation.

The additives are advantageously employed in functionally equivalent amounts known to those skilled in the art. For example, the amount of antioxidant employed is that amount which prevents the polymer or polymer blend from undergoing oxidation at the temperatures and environment employed during storage and ultimate use of the polymers. Such amount of antioxidants is usually in the range of from 0.01 to 10, preferably from 0.02 to 5, more preferably from 0.03 to 2 percent by weight based upon the weight of the polymer or polymer blend. Similarly, the amounts of any of the other enumerated additives are the functionally equivalent amounts such as the amount to render the polymer or polymer blend antiblocking, to produce the desired amount of filler loading to produce the desired result, to provide the desired color from the colorant or pigment.

Also included as a potential component of the polymer compositions used in the present invention are various organic and inorganic fillers, the identity of which depends upon the type of application for which the composition is to be utilized. The fillers can be advantageously employed in amounts up to 90 percent by weight based on the weight of the polymer blend.

Representative examples of such fillers include organic and inorganic fibers such as those made from asbestos, boron, graphite, ceramic, glass, metals (such as stainless steel) or polymers (such as aramid fibers) talc, carbon black, carbon fibers, calcium carbonate, alumina trihydrate, glass fibers,

marble dust, cement dust, clay, feldspar, silica or glass, fumed silica, alumina, magnesium oxide, magnesium hydroxide, antimony oxide, zinc oxide, barium sulfate, aluminum silicate, calcium silicate, titanium dioxide, titanates, aluminum nitride, B<sub>2</sub>O<sub>3</sub>, nickel powder or chalk.

Other representative organic or inorganic, fiber or mineral, fillers include carbonates such as barium, calcium or magnesium carbonate; fluorides such as calcium or sodium aluminum fluoride; hydroxides such as aluminum hydroxide; metals such as aluminum, bronze, lead or zinc; oxides such as aluminum, antimony, magnesium or zinc oxide, or silicon or titanium dioxide; silicates such as asbestos, mica, clay (kaolin or calcined kaolin), calcium silicate, feldspar, glass (ground or flaked glass or hollow glass spheres or microspheres or beads, whiskers or filaments), nepheline, perlite, pyrophyllite, talc or wollastonite; sulfates such as barium or calcium sulfate; metal sulfides; cellulose, in forms such as wood or shell flour; calcium terephthalate; and liquid crystals. Also included are the various classes of fillers that act as anti-microbial agents. Mixtures of more than one such filler may be used as well.

Processing aids, which are also referred to herein as plasticizers, can also be included in the compositions of the present invention., and include the phthalates, such as dioctyl phthalate and diisobutyl phthalate, natural oils such as lanolin, and paraffin, naphthenic and aromatic oils obtained from petroleum refining, and liquid resins from rosin or petroleum feedstocks. Exemplary classes of oils useful as processing aids include white mineral oil (such as Kaydol™ oil (available from and a registered trademark of Witco), and Shellflex™ 371 naphthenic oil (available from and a registered trademark of Shell Oil Company). Another suitable oil is Tuflo™ oil (available from and a registered trademark of Lyondell).

A nucleating agent is optionally added to control the size of foam cells. Preferred nucleating agents include inorganic substances such as calcium carbonate, talc, clay, titanium dioxide, silica, barium stearate, calcium stearate, diatomaceous earth, mixtures of citric acid and sodium bicarbonate. When used, the amount of nucleating agent employed advantageously ranges from 0.01 to 5 parts by weight per hundred parts by weight of a polymer resin.

In the manufacture of foams, a stability control agent (also known as permeability modifier) is optionally added to the present foam to enhance dimensional stability. Preferred agents include amides and esters of C10-24 fatty acids. Such agents are seen in U.S. Pat. Nos. 3,644,230 and 4,214,054. Esters may also reduce static during and after foam manufacture. Most preferred agents include stearyl stearamide, glyceromonostearate, glycerol monobehenate, and sorbitol monostearate. When used, such stability control agents are typically employed in an amount ranging from > 0 to 10 parts per hundred parts of the polymer.

The compositions comprise from 0.5 to 100, preferably from 5 to 100, and most preferably from 10 to 100 weight percent of one or more crosslinkable substantially random interpolymers.

The crosslinkable substantially random interpolymers contain from 0.5 to 65, preferably from 1 to 50, and most preferably from 1 to 45 mole percent of polymer units derived from one or more vinyl aromatic monomers, especially styrene; and from 1 to 99, preferably from 20 to 98 and most preferably from 30 to 98 mole percent of polymer units derived from ethylene or ethylene in combination with one or more C<sub>4</sub>-C<sub>20</sub>  $\alpha$ -olefins; and from 0.5 to 80, preferably from 1 to 50 and most preferably from 1 to 45 mole percent of polymer units derived from propylene; and, optionally from 0 to 20 mole percent of polymer units derived from one or more of ethylenically unsaturated polymerizable monomers, such as a diene.

The blend compositions can also comprise from 0.5 to 99.5, preferably from 0 to 95, and most preferably from 0 to 90 weight percent of one or more thermoplastics other than Component 1.

The blend compositions can also comprise from 0 to 90, preferably from 0 to 80, and most preferably from 0 to 70 weight percent of one or more fillers.

Specifically: (1) crosslinked 64/6/30 and 71/5/24 wt percent EPS resins are soft and have high UST; (2) crosslinked 82/11/7 and 81/5/14 wt percent EPS resins are soft, have good low T properties (because of low T<sub>g</sub>), high UST, and additionally may be paintable or printable.

The following examples are to illustrate this invention and do not limit it.

#### EXAMPLES

Melt Flow Measurements: Unless otherwise stated, the molecular weight of the polymer compositions for use in the present invention was conveniently indicated using a melt index measurement according to ASTM D-1238, Condition 190°C/2.16 kg (formally known as "Condition (E)" and also known as I<sub>2</sub>) was determined.

Thermal Mechanical Analysis (TMA): Upper service temperature was determined from a thermal mechanical analyzer (Perkin-Elmer TMA 7 series) scanned at 5 °C/min and a load of 1 Newton and defined as the point at which the probe penetrates 1 mm into the sample.

Nomenclature: 70/30 ES refers to an ESI resin comprising 70 wt percent ethylene & 30 wt percent styrene; 71/5/24 EPS refers to a terpolymer comprising 71 wt percent ethylene, 5 wt percent propylene & 24 wt percent styrene

Blends of various ethylene-propylene-styrene (EPS) terpolymers, ethylene-styrene interpolymers (ESI) and polyolefin elastomer (POE) with dicumyl peroxide were made without reacting the peroxide. Hercules DiCup R (>99.7 percent active) was used with all the resins, except with the 71/5/24 resin which involved the use of Luperox 500R (> 99 percent active). The pellets of polymer were melted using a Haake Rheometer & Rheomix 600 bowl initially at 20 RPM for 3

minutes. Peroxide was then added and the speed was ramped up to 50 RPM. The temperature setpoint was adjusted to maintain melt temperature less than 125°C (+/- 5°C). The entire mixing lasted at least 8 minutes. Less than 40 grams of each sample were collected. The polymers were also processed on the Haake without any peroxide. The properties of the various polymers were as shown in Table 2 :

The polymers were prepared using the following polymerization procedure.

Preparation of Ethylene/Propylene/Styrene Interpolymers Used in Examples and Comparative Experiments of Present Invention

The interpolymers were prepared in a continuously operating loop reactor. An Ingersoll-Dresser twin screw pump provided the mixing. The reactor ran liquid full at 475 psig (3,275 kPa). Raw materials and catalyst/cocatalyst flows were fed into the reactor through injectors and Kenics static mixers in the loop reactor piping. From the discharge of the loop pump, the process flow goes through two shell and tube heat exchangers before returning to the suction of the loop pump. Upon exiting the last exchanger, loop flow returned through the injectors and static mixers to the suction of the pump. A second monomer/feed injector and mixer was used if available. Heat transfer oil or tempered water was circulated through the exchangers' jacket to control the loop temperature. The exit stream of the loop reactor was taken off between the two exchangers. The flow and solution density of the exit stream was measured by a Micro-Motion<sup>TM</sup> mass flow meter.

Solvent was injected to the reactor primarily as part of the feed flow to keep the ethylene in solution. A split stream from the pressurization pumps prior to ethylene injection was taken to provide a flush flow for the loop reactor pump seals. Additional solvent was added as a diluent for the catalyst. Feed solvent was mixed with uninhibited styrene monomer on the suction side of the pressurization pump. The pressurization pump supplied solvent and styrene to the reactor at approximately 650 psig (4,583 kPa). Fresh styrene flow was measured by a Micro-Motion<sup>TM</sup> mass flow meter, and total solvent/styrene flow was measured by a separate Micro-Motion<sup>TM</sup> mass flow meter. Ethylene was supplied to the reactor at approximately 690 psig (4,865 kPa). The ethylene stream was measured by a Micro-Motion<sup>TM</sup> mass flow meter. A flow meter /controller was used to deliver hydrogen into the ethylene stream at the outlet of the ethylene control valve.

The ethylene/hydrogen mixture was at ambient temperature when it was combined with the solvent/styrene stream. The temperature of the entire feed stream as it entered the reactor loop was lowered to approximately 2°C by a glycol cooled exchanger. Preparation of the three catalyst components took place in three separate tanks. Fresh solvent and concentrated catalyst/cocatalyst/secondary co-catalyst premix were added and mixed into their respective run tanks and fed into the reactor via a variable speed Pulsafeeder<sup>TM</sup> diaphragm pumps. As previously

explained, the three component catalyst system entered the reactor loop through an injector and static mixer into the suction side of the twin screw pump. The raw material feed stream was also fed into the reactor loop through an injector and static mixer upstream of the catalyst injection point or through a feed injector/mixer between the two exchangers, if available.

5 Polymerization was stopped with the addition of catalyst kill (water) into the reactor product line after the Micro-Motion™ mass flow meter measuring the solution density. A static mixer in the line provided dispersion of the catalyst kill and additives in the reactor effluent stream. This stream next entered post reactor heaters that provided additional energy for the solvent removal flash. This flash occurred as the effluent exited the post reactor heater and the pressure was dropped from 475  
10 psig (3,275 kPa) down to approximately 450 mmHg (60 kPa) of absolute pressure at the reactor pressure control valve.

This flashed polymer entered the devolatilization section of the process. The volatiles flashing from the devolatilization were condensed with a glycol jacketed exchanger, passed through vacuum pump, and were discharged to vapor/liquid separation vessel. In the first stage vacuum  
15 system, solvent/styrene were removed from the bottom of this vessel as recycle solvent while unreacted ethylene exhausted from the top. The ethylene stream was measured with a Micro-Motion™ mass flow meter. The measurement of vented ethylene plus a calculation of the dissolved gases in the solvent/styrene stream were used to calculate the ethylene conversion. The polymer and remaining solvent was pumped with a gear pump to a final devolatilizer. The pressure in the second  
20 devolatilizer was operated at approximately 10 mmHg (1.4 kPa) absolute pressure to flash the remaining solvent. The dry polymer (< 1000 ppm total volatiles) was pumped with a gear pump to an underwater pelletizer with spin-dried, and collected. The preparation conditions for each sample were varied to produce the specific interpolymers summarized in Table 1.

Table 1

Sample No.	Wt percent composition	I <sub>2</sub> (dg/min)	wt percent E	Wt percent P	Wt percent S	Mol percent E	Mol percent P	Mol percent S	percent crystallinity
ES 1	70/30 ES*	1	70	-	30	89.7	-	10.3	15
EPS 1	71/5/24 EPS	1.0	71	5	24	87.9	4.1	8.0	16
EPS 2	64/6/30 EPS	0.8	64	6	30	84.1	5.3	10.6	8
EPS 3	70/16/14 EPS	1.0	70	16	14	82.9	12.6	4.5	12
EPS 4	74/24/2 EPS	0.6	74	24	2	81.7	17.7	0.6	17
ES 2	31/69 ES		31	-	69	62.5	-	37.5	
EPS 5	28/6/66 EPS	0.9	28	6	66	56.3	8.0	35.7	
POE 1	POE VP8770*	1	72	-	-	91.0	-	-	22
EPS 6	82/11/7 EPS	1.0	82	11	7	89.9	8.0	2.1	29
EPS 7	81/5/14 EPS	1.0	81	5	14	91.9	3.8	4.3	30

POE VP8770 is an ethylene/octene polyolefin elastomer, AFFINITY\* VP8770 (a product and trademark of The Dow Chemical Company) having a melt index (I<sub>2</sub>) of 1.0 g/10 min and a density of 0.885 g/cm<sup>3</sup>.



The samples from the Haake were run in a Monsanto Oscillating Disk Rheometer (ODR) at 177°C and the torque was measured over time. Gel content was measured on these samples, in accordance with ASTM D-2765-84. Compression molded specimens were also made from the Haake blends (to fully react peroxide) and Haake processed polymers. 10 grams of sample were placed in a 3" X 2" X 70 mils chase which in turn was placed between two mylar sheets on plates. A Carver Press and the conditions described below were used to mold the samples.

**Table 2**

Temperature (°C)	Oven/Press	Pressure (psi)	Time (minutes)
120	1	5000	2
120	1	15000	4
23	1	5000	2
23	1	15000	4
180	2	15000	15
23	2	15000	6

Upper service temperature (UST), Shore A and tensile properties were measured on compression molded specimens. UST was determined using a Perkin- Elmer TMA-7 instrument with a one millimeter diameter probe. A sample, 3 mm thick x 5 mm in diameter, was penetrated with a force of one newton (102.4g) as the temperature was increased at a rate of 5°C /minute. The temperatures were reported at 0.2 mm and 1 mm probe positions. Dogbones were cut from the compression molded specimens using ASTM 1708 die and punch press, and tensile properties were measure using an Instron machine.

Table 3

Sample No.	Torque (in-lb) 90 s/Max/900	UST (°C) 0.2/ 1.0 mm	Hardness Shore A	Break Stress (psi)	Elongation (percent)	Toughness (ft lb/cu in)	Gels (percent)
ES 1+	4.1	61 / 74	75	3086	644	685	0.4
EPS 1	3.9 - 3.3	60 / 72	80	3326	741	924	
EPS 2		45 / 55	66	1381	676	345	0.3
EPS 3	3.2 - 2.7	48 / 57	78	2374	1224	999	0.3
EPS 4	4.1 - 3.8	51 / 59	73	1435	1221	762	0.3
ES 2+	5.6 - 4.0	54 / 69	65	3247	275	332	0.8
EPS 5	6.1 - N/A	48 / 65	59	1974	376	224	
POE VP8770+	3.9 - 3.5	79 / 88	81	3040	880	1136	0.4
EPS 6	3.1 - 2.9	80 / 86	87	2914	809	1069	0.1
EPS 7	4.1/-4.4	84 / 90	84	3399	673	1018	0.3
<b>1.5 phr DiCup R*</b>							
ES 1+	8.4/33/29	62 / 89	79	3068	639	680	84.3
EPS 1	6.4/21/19	64 / 129	80	2201	572	469	
EPS 2	11.6/42/39	48 / >190	60	1797	750	453	88.5
EPS 3	7.4/37/37	51 / >190	65	2562	944	728	90.9
EPS 4	15.9/74/N/A	>190 / >190	72	1980	861	585	99.3
ES 2+	6.6/10/7	49 / 67	60	1855	261	179	
EPS 5	9.4/17/10	48 / 67	54	981	375	141	13.6
POE VP8770+	9.7/57/57	>190 / >190	83	2822	675	751	96.8
EPS 6	9.7/51/51	85 / >190	87	3016	680	880	92.9
EPS 7	9.6/46/46	81 / >190	86	3298	625	914	91.1
<b>3.0 phr DiCup R*</b>							
ES 1+	12.3/48/44	>190 / >190	77	2351	563	467	95.5
EPS 1	10.0/38/36	>190 / >190	78	2094	531	407	
EPS 2	16.1/70/67	>190 / >190	N/A	2246	739	501	97.8
EPS 3	11.0/73/73	>190 / >190	66	2026	701	453	
EPS 4	23.2/94/91	>190 / >190	60	650	387	126	99.3
ES 2+	12.0/25/14	48 / 70	55	1699	344	204	75.1
EPS 5	11.0/30/18	43 / 72	51	660	381	112	80.5
POE VP8770+	17.3/79/79	>190 / >190	84	2349	569	564	99.9
EPS 6	35.0/83/78	>190 / >190	87	2815	530	585	98.9
EPS 7	17.4/83/83	>190 / >190	83	3253	548	762	97.3

\*No peroxide

+Not an example of the present invention

## CLAIMS

## 1. A polymer composition comprising

- 1) from 0.5 to 100 percent by weight (based on the combined weight of Components 1, 2 and 3) of one or more crosslinkable substantially random interpolymers comprising;
  - a) from 0.5 to 65 mol percent of polymer units derived from at least one vinyl aromatic monomer,
  - b) from 1 to 99 mol percent of polymer units derived from ethylene or ethylene in combination with one or more C<sub>4</sub>-C<sub>20</sub>  $\alpha$ -olefins;
  - c) from 0.5 to 80 mol percent of polymer units derived from propylene; and
  - d) from 0 to 20 mol percent of polymer units derived from one or more of ethylenically unsaturated polymerizable monomers other than those derived from (a) and (b); and;
- 2) from 0 to 99.5 percent by weight (based on the combined weight of Components 1, 2 and 3) of one or more thermoplastics other than Component 1.
- 3) from 0 to 90 percent by weight (based on the combined weight of Components 1, 2 and 3) of one or more fillers.

## 2. The polymer composition of Claim 1 comprising

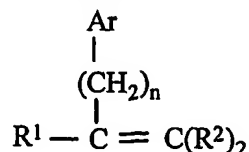
- 1) from 5 to 100 percent by weight (based on the combined weight of Components 1, 2 and 3) of one or more crosslinkable substantially random interpolymers comprising;
  - a) from 1 to 50 mol percent of polymer units derived from at least one vinyl aromatic monomer,
  - b) from 20 to 98 mol percent of polymer units derived from ethylene or ethylene in combination with one or more C<sub>4</sub>-C<sub>20</sub>  $\alpha$ -olefins;
  - c) from 1 to 50 mol percent of polymer units derived from propylene; and
- 2) from 0 to 95 percent by weight (based on the combined weight of Components 1, 2 and 3) of one or more thermoplastics other than Component 1
- 3) from 0 to 80 percent by weight (based on the combined weight of Components 1, 2 and 3) of one or more fillers.

## 3. The polymer composition of Claim 1 comprising

- 1) from 10 to 100 percent by weight (based on the combined weight of Components 1, 2 and 3) of one or more crosslinkable substantially random interpolymers

comprising;

- a) from 1 to 45 mol percent of polymer units derived from at least one said vinyl aromatic monomers represented by the following formula;



wherein  $\text{R}^1$  is selected from the group of radicals consisting of hydrogen and alkyl radicals containing three carbons or less, and Ar is a phenyl group or a phenyl group substituted with from 1 to 5 substituents selected from the group consisting of halo,  $\text{C}_{1-4}$ -alkyl, and  $\text{C}_{1-4}$ -haloalkyl and n is from 0 to 4;

- b) from 30 to 98 mol percent of polymer units derived from ethylene;
- c) from 1 to 45 mol percent of polymer units derived from propylene; and
- 2) from 0 to 90 percent by weight (based on the combined weight of Components 1, 2 and 3) of one or more thermoplastics other than Component 1 comprising one or more ethylene and/or  $\alpha$ -olefin homopolymers and interpolymers, polypropylene homopolymers and copolymers, thermoplastic olefins (TPOs), styrene - diene copolymers, styrenic homopolymers and copolymers, elastomers, vinyl halide polymers, and engineering thermoplastics; and
- 3) from 0 to 70 percent by weight (based on the combined weight of Components 1, 2 and 3) of one or more fillers.
4. The polymer composition of Claim 3 wherein said substantially random interpolymer comprises polymer units derived from ethylene, propylene and styrene.
5. An expandable composition comprising
- (A) at least one blowing agent; and
  - (B) the polymer composition of Claim 1
5. The polymer composition of Claim 1 in the form of a film, sheet or as a component of a multilayered structure resulting from calendering, blowing, casting, or (co-)extrusion operations.
- 6.. The polymer composition of Claim 1 in the form of fabricated articles produced by compression molding, injection molding, blow molding, profile extrusion, or thermoforming operations.

7. The polymer composition of Claim 1 in the form of a fiber or emulsion.
8. The polymer composition of Claim 1 in the form of an adhesive, adhesive formulation or sealant composition.
9. The polymer composition of Claim 1 in the form of wire and cable insulation, gasket, hose, boots and shoes for high temperature use, and automobile parts and trim.
10. A foam composition comprising the polymer composition of Claim 1.
11. The foam composition of Claim 11 in the form of shoe soles, pipe insulation, furniture, athletic sponge pads, sound deadening panels, and heat insulation.
12. A thermoplastic vulcanizate comprising: the polymer composition of Claim 1; wherein said one or more thermoplastics other than Component 1 is present in an amount of from 5 to 95 percent by weight (based on the combined weight of Components 1, 2 and 3) and comprises one or more ethylene, propylene and/or C<sub>4</sub>-C<sub>20</sub>  $\alpha$ -olefin homopolymers and interpolymers, or one or more thermoplastic polyolefins (TPOs).
14. A process for making a thermoplastic vulcanizate comprising:
  - (a) polymerizing at least one  $\alpha$ -olefin with at least one viny aromatic compound and optionally at least one diene in the presence of a constrained geometry catalyst to form a substantially random interpolymer;
  - (b) intimately mixing the substantially random interpolymer with at least one thermoplastic polyolefin at a temperature above the melting or softening point of the thermoplastic polyolefin;
  - (c) providing to the intimate mixture an agent for curing the substantially random interpolymer;
  - (d) simultaneously curing the substantially random interpolymer and compounding the intimate mixture to form a thermoplastic vulcanizate..

15. The composition of Claim 1 or fabricated article of claims 6-13 in which the substantially random interpolymer component has a crosslinked gel content of 50 weight percent or less.
16. The composition of Claim 1 or fabricated article of claims 6-13 in which the substantially random interpolymer component has a crosslinked gel greater than 50 percent.
17. The foam of Claims 11 or 12, wherein the foam has an open cell content of 30 volume percent or less.
18. The foam of Claims 11 or 12, wherein the foam has an open cell content of greater than 30 volume percent.
19. The foam of Claims 11 or 12, wherein the foam has defined therein a multiplicity of channels, the channels being free of direction with respect to the longitudinal extension of the foam and enhancing or accelerating a gaseous permeation exchange wherein blowing agent exits from the foam and air enters into the foam.
20. The foam of Claims 11 or 12, wherein the foam is in the shape of a sheet or plank with a thickness of at least 0.5 millimeters and width of at least 5 millimeters, or a rod having a diameter of at least 5 millimeters.
21. The foam of Claims 11 or 12, wherein the foam is shaped as thermoplastic foam beads or as expanded and fused thermoplastic foam beads.
22. The foam of Claims 11 or 12, wherein the foam is a unitary foam structure that is a coalesced strand foam.
23. A process for making a polymer foam; which comprises;
  - (i) converting the grafted blend composition of Claim 1 into a polymer melt;

- (ii) introducing, at an elevated pressure, at least one blowing agent into the polymer melt to form a foamable gel, the blowing agent being present in a total amount of from 0.05 to 5.0 gram-moles per kilogram of polymers contained in the polymer melt;
- (iii) cooling the foamable gel to an optimum temperature; and
- (iv) extruding the foamable gel from step iii through a die to a region of lower pressure to form a foam.

24. The process of claim 23, wherein said die is a multi-orifice die with orifice spacing sufficient to ensure that contact between surfaces of adjacent streams of extrudate occurs during foaming in the region of lower pressure, the contact being sufficient to ensure that the contacting surfaces adhere to one another with sufficient adhesion to result in a unitary foam structure that is a coalesced strand foam.
25. The process of claim 23, wherein steps (iii) and (iv) constitute an intermittent process that employs an accumulating extruder means to first accumulate foamable gel in a holding zone maintained at a temperature and pressure which does not allow the gel to foam and then periodically eject accumulated gel through the die.
26. The process of claim 23, wherein the optimum temperature is a temperature at which foaming does not occur and step (iv) is modified such that no foaming occurs and the resulting extrudate is pelletized to form expandable thermoplastic beads.
27. A process for making a foam in the form of thermoplastic foam beads, which process comprises sequential steps (i) – (v);
- (i) converting the grafted blend composition of Claim 1 into a polymer melt;
  - (ii) cooling and granulating the polymer melt to form discrete resin particles;
  - (iii) creating a suspension by dispersing the resin particles in a liquid medium in which they are substantially insoluble;
  - (iv) introducing, at an elevated temperature and pressure, at least one blowing agent (and optionally a cross-linking agent) into the suspension to form resin particles having a blowing agent incorporated therein; and

- (v) rapidly discharging product formed in step iv into an atmosphere that promotes converting the product into foam beads.